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PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
BEFORE THE BOARD OF APPEALS AND INTERFERENCES

DN A01463

In re application of

Brian Michael Bridgewater, et al..

Paper No.: ?

Serial No. 10/700,078

Group Art Unit: 1714

Filed: November 3, 2003

Examiner: V. Ronesi

For: AQUEOUS ACRYLIC EMULSION POLYMER COMPOSITION

Honorable Commissioner for Patents

P.O. Box 1450

Alexandria, VA 22313-1450

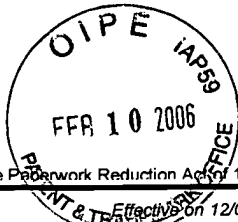
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Dear Sir:

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Date February 8, 2006

Signature Shelley Dalmy



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Effective on 12/08/2004.
Fees pursuant to the Consolidated Appropriations Act, 2005 (H.R. 4818).**FEE TRANSMITTAL**
For FY 2005☐ Applicant claims small entity status. See 37 CFR 1.27**TOTAL AMOUNT OF PAYMENT** (\$) 500.00**Complete if Known**

Application Number	10/700,078
Filing Date	November 3, 2003
First Named Inventor	Brian M. Bridgewater et al
Examiner Name	V. Ronesi
Art Unit	1714
Attorney Docket No.	A01463

METHOD OF PAYMENT (check all that apply)☐ Check ☐ Credit Card ☐ Money Order ☐ None ☐ Other (please identify): _____☒ Deposit Account Deposit Account Number: 18-1850 Deposit Account Name: Rohm and Haas Company

For the above-identified deposit account, the Director is hereby authorized to: (check all that apply)

☒ Charge fee(s) indicated below ☐ Charge fee(s) indicated below, except for the filing fee☒ Charge any additional fee(s) or underpayments of fee(s) under 37 CFR 1.16 and 1.17 ☒ Credit any overpayments**WARNING:** Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.**FEE CALCULATION****1. BASIC FILING, SEARCH, AND EXAMINATION FEES**

Application Type	FILING FEES		SEARCH FEES		EXAMINATION FEES		Fees Paid (\$)
	Fee (\$)	Small Entity Fee (\$)	Fee (\$)	Small Entity Fee (\$)	Fee (\$)	Small Entity Fee (\$)	
Utility	300	150	500	250	200	100	
Design	200	100	100	50	130	65	
Plant	200	100	300	150	160	80	
Reissue	300	150	500	250	600	300	
Provisional	200	100	0	0	0	0	

2. EXCESS CLAIM FEES**Fee Description**

Each claim over 20 (including Reissues)

Fee (\$)	Small Entity Fee (\$)
50	25

Each independent claim over 3 (including Reissues)

200	100
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Multiple dependent claims

360	180
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Total Claims	Extra Claims	Fee (\$)	Fee Paid (\$)
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- 20 or HP = _____ x _____ = 0

HP = highest number of total claims paid for, if greater than 20.

Indep. Claims	Extra Claims	Fee (\$)	Fee Paid (\$)
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- 3 or HP = _____ x _____ = 0

HP = highest number of independent claims paid for, if greater than 3.

3. APPLICATION SIZE FEE

If the specification and drawings exceed 100 sheets of paper (excluding electronically filed sequence or computer listings under 37 CFR 1.52(e)), the application size fee due is \$250 (\$125 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).

Total Sheets	Extra Sheets	Number of each additional 50 or fraction thereof	Fee (\$)	Fee Paid (\$)
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- 100 = _____ / 50 = _____ (round up to a whole number) x _____ = _____

4. OTHER FEE(S)

Non-English Specification, \$130 fee (no small entity discount)

Fees Paid (\$)Other (e.g., late filing surcharge): Appeal Brief500.00**SUBMITTED BY**

Signature		Registration No. (Attorney/Agent) 31,064	Telephone 215-592-2171
Name (Print/Type)	Robert Stevenson	Date February 8, 2006	

This collection of information is required by 37 CFR 1.136. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 30 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

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GROUP UNIT: 1714

APPEAL NO. _____

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
BEFORE THE BOARD OF APPEALS AND INTERFERENCES

APPELLANTS' BRIEF

Brian Michael Bridgewater, et al.

Application for Patent Filed: November 3, 2003

Serial No.: 10/700,078

AQUEOUS ACRYLIC EMULSION POLYMER COMPOSITION

Robert Stevenson
Attorney for Appellants

V. Ronesi
Examiner

Enclosed:

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Filing Fee via Fee Transmittal Form (in duplicate)

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PATENT

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DN A01463

In re application of

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Honorable Commissioner for Patents

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Alexandria, VA 22313-1450

BRIEF FOR APPELLANTS

This is an appeal from the final rejection by the Examiner of September 15, 2005 rejecting claims 1-7. Appellants filed a Notice of Appeal pursuant to 37 C.F.R. 1.191 on December 8, 2005.

An authorization to charge payment of the fee for the filing of the Appeal Brief to Deposit Account 18-1850 is also enclosed.

REAL PARTY IN INTEREST [37 C.F.R. § 1.192(c)(1)]

The real party in interest is Rohm and Haas Company, 100 Independence Mall West, Philadelphia, PA 19106-2399.

RELATED APPEALS AND INTERFERENCES [37 C.F.R. § 1.192(c)(2)]

There are no other related appeals or interferences that will directly affect or be directly affected or have a bearing on the Board's decision in the pending appeal.

STATUS OF CLAIMS [37 C.F.R. § 1.192(c)(3)]

The status of the claims is as follows:

Allowed claims	-	none
Claims objected to	-	none
Claims cancelled	-	none
Claims pending	-	1-7 and 10-14
Claims withdrawn from consideration	-	10-14
Claims rejected	-	1-7
Claims on appeal	-	1-7

STATUS OF AMENDMENTS

The rejected claims are set out in Appendix 1.

SUMMARY OF INVENTION

Appellants claim (claim 1) an aqueous coating composition comprising a pigment and an aqueous acrylic emulsion polymer comprising, as copolymerized units, from 50 to 99.75% by weight, based on dry polymer weight, monoethylenically unsaturated nonionic (meth)acrylic monomer and from 0.25 to 10% by weight, based on dry polymer weight, monoethylenically unsaturated acid monomer, said polymer having a glass transition temperature (T_g) of -10 °C to 35 °C wherein said

emulsion polymer is formed by emulsion polymerization at a temperature of from 70 °C to 99 °C in the presence of a thermal initiator, wherein said initiator is used in the amount of 0.3% to 0.4%, by weight, based on dry polymer weight, and wherein less than 0.15% by weight, based on dry polymer weight, of said initiator is present during the first 10%, by weight, based on dry polymer weight, of the conversion of monomers to said emulsion polymer; 0.001 to 0.05 moles of chain transfer agent/kg monomer; and a neutralizer, wherein said neutralizer is used in the amount of from 5% to 75%, on an equivalents basis, based on said monoethylenically unsaturated acid monomer, and wherein less than half of said neutralizer is present during the first 25%, by weight, based on dry polymer weight, of the conversion of monomers to said emulsion polymer.

ISSUES

- I. Whether appellants' invention of claims 1-7 is unpatentable under 35 USC 102(b) over US 5,731,377 to Friel ("Friel").
- II. Whether appellants' invention of claims 1-7 is obvious under 35 USC 103(a) over Friel.

THE REJECTIONS

Claims 1-7 stand finally rejected under 35 USC 102(b) as being unpatentable over Friel.

Claims 1-7 stand finally rejected under 35 USC 103(a) as being unpatentable over Friel.

The Examiner's Arguments

The Examiner asserts that claims 1-7 stand finally rejected under 35 USC 102(b) or, in the alternative, under 35 USC 103(a) as being unpatentable over the prior art as represented by Friel.

The examiner contends that the appellants' data, although clearly showing advantage for the inventive composition and process over those of the prior art, has not provided a perfect comparison with prior art systems. In particular, the data presented to illustrate improvement in scrub resistance properties derives from paints formulated with binders of the inventive polymers versus those of the comparable prior art method. The ingredients of the paint formulations are identical except for minor adjustments to the quantity of rheology modifier added to attain equal viscosities. The examiner, therefore, contends that the formulations are not identical and so comparative data for the inventive method versus that of the prior art are "not proper".

GROUPING OF CLAIMS

As to the rejections applied against claims 1-7 under 35 USC 102(a) and under 35 USC 103(a), it is appellants' intention for each ground of rejection that the rejected claims stand or fall together for the purposes of this Appeal. However, we reserve the right to file continuing applications on subject matter contained in various claims.

ARGUMENTS

Claims 1-7 are not unpatentable over Friel under 35 USC 102(b) because the data presented in the application demonstrates significant improvement for the inventive polymers over those of the prior art. Specifically, the applicants have shown that the data in their Table 4.1 (see Appellants' published patent specification; Exhibit D) refute the assumption that, on the basis of similarities in monomer compositions, it may be concluded that emulsion polymers made by a given process are the same as, or obvious in light of, emulsion polymers made by another process. The applicants have pointed out that large differences are seen in the scrub resistance data in Table 4.1 for 6 polymers made by 6 different processes,

using the same monomer compositions but the best ones are those that fall within the scope of their claims. All other formulation components were held constant for the samples tested, except, as the Examiner has correctly noted, the levels of rheology modifier employed in the formulation. The paints have been formulated to comply with the industry standard scrub test procedures (ASTM D 2486-00, attached, exhibit B) and the tests performed in a manner accepted by the industry to optimize the validity of comparative data.

The issue here is the requirement of the test to provide paint films of equal thickness. This is because the scrub resistance test is a wet abrasion “cut through” test which involves wearing through the entire thickness of the (white) coating until the (black) substrate becomes clearly visible. To one skilled in the art and familiar with this test, it is clear that the test has a film thickness dependence to it, although this was not understood by the examiner when assessing the data. In a Dec 8th, 2005, interview with the examiners, the appellants provided the full written test procedure, after which the Examiners concluded that there is indeed a dry film thickness dependence on the number of scrub cycles required to reach the endpoint of the test. Thus, in comparing data between waterborne polymer compositions, the dry film thickness needs to be kept constant between samples. The Examiners therefore stated that it was in error to state in the Advisory Action that “scrub resistance is a property of the surface of a coating and not the bulk”.

The appellants pointed out that for a valid comparison of scrub resistance between two wet polymer compositions, the compositions need to be applied at equal wet film thicknesses to provide equal dry film thicknesses, but that this could only occur if the rheology profile was the same between samples. Because different polymer compositions can have different responses to rheology modifiers, it is inevitable that slightly different quantities of rheology modifier are required to produce applied films of equal wet film thickness.

To ensure optimal comparisons in scrub resistance data between different polymer compositions, the applicants adjusted rheology of the wet compositions in order to provide films of equal film thickness. This is the standard procedure in the industry since it provides a better comparison than comparing films of unequal film thickness, as demonstrated by the Declaration of Matthew S. Gebhard (Appendix B) that was submitted during *ex parte* prosecution below.

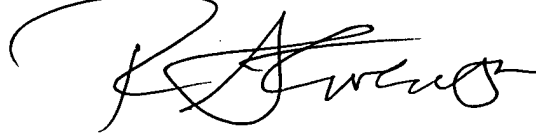
These scrub resistance data demonstrate that compared to the prior art, the inventive composition has unexpected good and unobvious scrub resistance compared to the prior art.

Conclusion

Appellants respectfully submit that the present invention as defined by claims 1-7 is not anticipated under 35 U.S.C. 102(b) or 35 U.S.C. 103(a) over Friel. On the basis of the data presented in the application, one must only conclude that the nature of products of emulsion polymer processes are strongly dependent on process specifics, a fact well known to those skilled in the art. In light of these data, applicants submit that there is no basis to assume that the products of Friel are the same as those produced by the inventive process. Neither does Friel provide any motivation to the practitioner to modify his processes in manner provided by the current application. The comparative examples shown in the application are representative of the prior art including Friel, and a more fair comparison is presented *via* the use of the rheology modifier adjustment to give equal viscosity and therefore equal coating thickness (prior art *vs.* inventive samples).

Appellants respectfully request the Board to reverse the Examiner's rejections and enter a Notice of Allowance. The Commissioner is hereby authorized to charge any additional fee which may be required, or to credit any overpayments to Deposit Account 18-1850.

Respectfully submitted,

A handwritten signature in black ink, appearing to read 'R. Stevenson', with a large, sweeping initial 'R'.

ROBERT W. STEVENSON
Attorney for Appellants
Registration No. 31,064
Telephone No.: 215-592-2171

February 8, 2006
Rohm and Haas Company
100 Independence Mall West
Philadelphia, PA 19106-2399

APPENDIX A

CLAIMS 1-7

1. An aqueous coating composition comprising a pigment and an aqueous acrylic emulsion polymer comprising, as copolymerized units, from 50 to 99.75% by weight, based on dry polymer weight, monoethylenically unsaturated nonionic (meth)acrylic monomer and from 0.25 to 10% by weight, based on dry polymer weight, monoethylenically unsaturated acid monomer, said polymer having a glass transition temperature (T_g) of $-10\text{ }^{\circ}\text{C}$ to $35\text{ }^{\circ}\text{C}$ wherein said emulsion polymer is formed by emulsion polymerization at a temperature of from $70\text{ }^{\circ}\text{C}$ to $99\text{ }^{\circ}\text{C}$ in the presence of a thermal initiator, wherein said initiator is used in the amount of 0.3% to 0.4%, by weight, based on dry polymer weight, and wherein less than 0.15% by weight, based on dry polymer weight, of said initiator is present during the first 10%, by weight, based on dry polymer weight, of the conversion of monomers to said emulsion polymer; 0.001 to 0.05 moles of chain transfer agent/kg monomer; and a neutralizer, wherein said neutralizer is used in the amount of from 5% to 75%, on an equivalents basis, based on said monoethylenically unsaturated acid monomer, and wherein less than half of said neutralizer is present during the first 25%, by weight, based on dry polymer weight, of the conversion of monomers to said emulsion polymer.
2. An aqueous coating composition comprising a pigment and an aqueous acrylic emulsion polymer comprising, as copolymerized units, from 50 to 99.75% by weight, based on dry polymer weight, monoethylenically unsaturated nonionic (meth)acrylic monomer and from 0.25 to 10% by weight, based on dry polymer weight, monoethylenically unsaturated

acid monomer, said polymer having a Tg of -10°C to 35°C wherein said emulsion polymer is formed by emulsion polymerization at a temperature of from 70°C to 99°C in the presence of a thermal initiator, wherein said initiator is used in the amount of 0.05 to 0.3%, by weight, based on dry polymer weight, and wherein less than half of said initiator is present during the first 10%, by weight, based on dry polymer weight, of the conversion of monomers to said emulsion polymer, and a neutralizer, wherein said neutralizer is used in the amount of from 5% to 75%, on an equivalents basis, based on said monoethylenically unsaturated acid monomer, and wherein less than half of said neutralizer is present during the first 25%, by weight, based on dry polymer weight, of the conversion of monomers to said emulsion polymer.

3. The aqueous coating composition of claim 1 or claim 2 wherein said aqueous acrylic emulsion polymer comprises, as copolymerized units based on dry polymer weight, from 50% to 99.65% by weight monoethylenically unsaturated nonionic (meth)acrylic monomer, from 0.1% to 12.5% by weight aldehyde reactive group-containing monomer, and from 0.25% to 10% by weight monoethylenically unsaturated acid monomer.
4. The aqueous coating composition of claim 1 or claim 2 further comprising from 2% to 40% by weight, based on the total dry polymer weight, of a second emulsion polymer that has a Tg of from 25°C to 150°C , wherein the Tg of said second polymer is at least 10°C higher than the Tg of said aqueous acrylic emulsion polymer.

5. The aqueous coating composition of claim 1 or claim 2 having a PVC of 15 to 38 and having VOC less than 5% by weight based on the total weight of the coating composition.
6. The aqueous coating composition of claim 1 or claim 2 having a PVC greater than 38 and having VOC less than 3% by weight based on the total weight of the coating composition.
7. The aqueous coating composition of claim 1 or claim 2 having a PVC of 15 to 85 and having VOC less than 1.7% by weight based on the total weight of the coating composition.

APPENDIX B – DECLARATION OF MATTHEW S. GEBHARD

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Atty Docket No.: A01463

In re application of: Brian Michael Bridgewater et al.

Confirmation No. 3734

Serial No.: 10/700,078

Group Art Unit: 1714

Filed: November 3, 2003

Examiner: Vickey Ronesi

For: Aqueous Coating Composition Comprising Emulsion Polymer Formed In The Presence of Thermal Initiator And Neutralizer

DECLARATION OF MATTHEW S. GEBHARD UNDER 37 C.F.R. §1.132

This declaration explains why the data presented in Table 4.1 of Patent Application Serial Number 10/700,078 is data representative of the constituent polymers of Examples 1 and 2 and Comparative Examples A-D.

The Declarant

(1) My name is Matthew S. Gebhard, and I reside at 158 Woodland Dr. Road, New Britain, PA 18901. I received my B.S. in Chemistry from San Francisco State University in 1985, and my PhD in Chemistry from Stanford University in 1990. I am a named inventor on this application.

(2) I have been employed by Rohm and Haas Company since 1990, most recently as a Senior Chemist in Coatings Applications. My primary job responsibility over that 15-year period was the experimental design of new emulsion polymers and their evaluation, specifically in their use in the Coatings industry. During that time, I performed many evaluations of emulsion polymers using the scrub machine apparatus and had others perform such evaluations under my direction, including evaluation of the emulsion polymers of this Patent Application.

The September 15, 2005 Office Action

(3) I reviewed this Office Action and understand that the Examiner rejected pending Claims 1-5 and 7-9 as obvious over Friel (US 5,731,377). In particular, the Examiner indicated that Examples 1 and 2, and Comparative Examples A, B, C, and D are not proper side-by-side examples since each one has a different amount of rheology modifier (Table 3.1, pages 19-20). As explained below, I believe the side-by-side comparisons are appropriate, and I believe that our Claims are unobvious over the earlier work of Friel.

Scrub Resistance Data (Number of Scrubs)

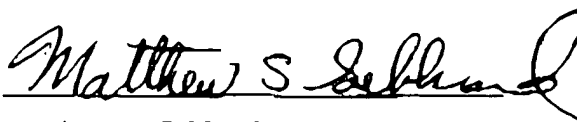
(4) The scrub resistance data presented in Table 4.1 in the Application is representative of the polymers used in Example 1 and 2, and Comparative Examples A-D. This is because the only other variable in these examples is the thickener used to bring about a constant viscosity. This is required in order to produce coatings of equal dry film thickness, which is required in order to provide a fair sample to sample comparison for coatings evaluated by the scrub machine apparatus.

(5) This still presents a fair comparison of the data for the polymers because, in my experience, and in my opinion, the thickener has no significant effect on the scrub resistance of a given paint formulation at a given film thickness, and is therefore not impacting the data presented in Table 4.1. The polymer (binder) has the dominant effect in controlling the scrub resistance of coatings of equal thickness.

Statement Under 28 U.S.C. §1746

(6) I declare that all statements made in this declaration of my own knowledge are true. I believe that all statements made herein on information and belief also are true. Furthermore, I understand that willful false statements and the like so made are punishable by fine or imprisonment, or both, under the United States Code, and such willful false statements may jeopardize the validity of any patent application or patent that may issue on this patent application.

Dated: 11-15-2005


Matthew S. Gebhard

APPENDIX C

Standard Test Method for Scrub Resistance of Wall Paints

– ASTM D 2486-00 (4 pages)



Designation: D 2486 – 00

~~Exhibit A (P. 1 of 4)~~

Standard Test Methods for Scrub Resistance of Wall Paints¹

This standard is issued under the fixed designation D 2486; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 These test methods cover a procedure for determining the resistance of wall paints to erosion caused by scrubbing, referred to herein after as "scrub resistance".

1.2 Two test methods are covered as follows:

1.2.1 *Test Method A*—Cycles-to-failure obtained on test paint.

1.2.2 *Test Method B*—Ratio expressed as a percentage of cycles-to-failure obtained on the test paint to that obtained on a concurrent run with a known reference paint.

1.3 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 ASTM Standards:

D 3924 Specification for Standard Environment for Conditioning and Testing Paint, Varnish, Lacquer, and Related Materials²

D 4213 Test Method for Scrub Resistance of Paints by Abrasion Weight Loss²

3. Summary of Test Method

3.1 In Test Method A, the test paint is applied to a black plastic panel. After curing, the coated panel is placed over a 12.7 wide by 0.25-mm thick (½-in. by 10-mil) shim and held in place on a drawdown plate in a washability machine by means of a gasketed frame. The coated panel is then scrubbed with a bristle brush and an abrasive scrub medium until the paint film is removed in one continuous thin line across the shim.

3.2 In Test Method B, the test paint and a reference paint are applied simultaneously perpendicular to the length of the black

plastic panel. After curing, the coated panel is placed over two 12.7 by 0.25-mm (½-in. by 10-mil) shims that are positioned under each coating. The coatings are then scrubbed with a bristle brush and an abrasive scrub medium until each paint film is removed in one continuous thin line across its own shim.

4. Significance and Use

4.1 Paints often become soiled especially near doorways, windows, and in work and play areas. These test methods cover the determination of the relative resistance of different paints to erosion when repeatedly scrubbed during the life of the paint.

4.2 Test Method D 4213 is a similar scrub resistance test using a weight-loss technique and reporting volumetric film erosion rates.

4.3 Test Method A measures scrub resistance by the traditional cycles-to-failure concept. Poor correlation in scrub testing can be attributable to among other things variations in the stiffness of the brush bristles, condition of washability tester, application and drying conditions. In an attempt to improve reproducibility, Test Method B has been developed.

5. Apparatus

5.1 Straight Line Washability Machine.

5.1.1 Accessory Apparatus: (see Figs. 1 and 2).

5.1.1.1 *Nylon Bristle Brush and Accessories*, (total weight 454 ± 10 g).

5.1.1.2 *Drawdown Plate*, 454 by 165 by 6.3 mm (17½ by 6½ by ¼ in.)

5.1.1.3 *Brass Shims*, 12.7- by 0.25-mm (½-in. by 10-mils). Its length can be fitted to the width of the drawdown plate.

5.2 *Film Applicator*, having 0.18-mm (7-mil) clearance and 6.25-mm (¼-in.) edge and width of 135 mm (5¼-in.).

6. Reagents and Materials

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests.

¹ These test methods are under the jurisdiction of ASTM Committee D-1 on Paint and Related Coatings, Materials, and Applications and is the direct responsibility of Subcommittee D01.42 on Architectural Coatings.

Current edition approved March 10, 2000. Published May 2000. Originally published as D 2486 – 66 T. Last previous edition D 2486 – 96.

² Annual Book of ASTM Standards, Vol 06.02.

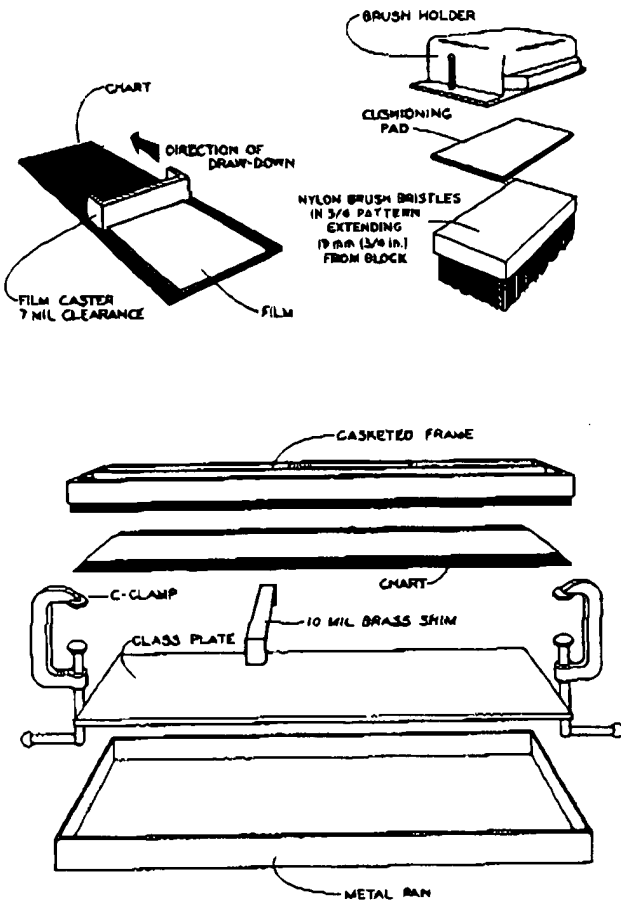


FIG. 1 Accessory Apparatus for Scrub Test

6.2 Black Plastic Panels.^{3,4}

6.3 Abrasive Scrub Medium.^{4,5}

6.3.1 Laboratory standardized abrasive scrub medium consisting of the following:

Water, distilled or deionized	49.4 ^a
Hydroxyethyl cellulose ^{4,6}	0.8
Ammonium hydroxide, 28 %	0.1
Detergent ^{4,7}	2.0
Trisodium phosphate, anhydrous	2.0
Silica ^{4,8}	45.0
Acetic acid (glacial)	0.7 ^b
Preservative ^{4,9}	0.1

^aAdjust to achieve viscosity of 110 to 120 Krebe units before use.

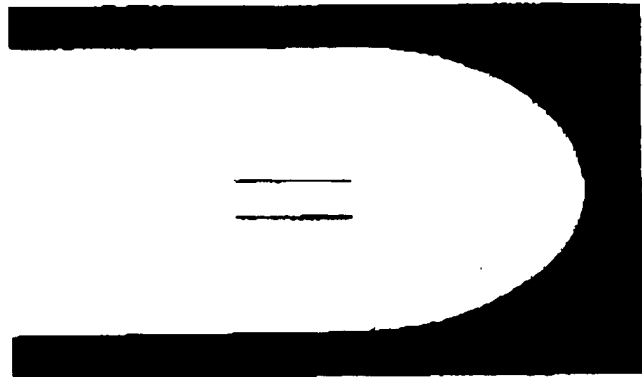
^bVary to achieve a pH of 9.5 to 10.

³ Dull black plastic panels, P-121-10N, 165 by 432 by 0.25 mm (6 1/4 by 17 in. by 10 mils) manufactured by the Leneta Co., 15 Whitney Rd., Mahwah, NJ 07430 were used in the original development of this standard in order to get the results in these test methods.

⁴ If you are aware of alternative suppliers, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.

⁵ The sole source of supply of the abrasive scrub medium known to the committee at this time is the Leneta Company.

⁶ The sole source of supply of cello size OP-4400, viscosity grade of HEC, known to the committee at this time is Union Carbide, Polymer Division, 318-24 Fourth Ave., So. Charleston, WV 25303.



Test Method A: Cycles to Failure on Test Panel



Test Method B: Ratio of Cycles to Failure of Test Panel and Reference Panel

FIG. 2 Accessory Apparatus for Scrub Test

6.4 Reference paint when using Test Method B.

7. Preparation of Apparatus

7.1 Washability Machine—The straight line washability machine should be leveled before use and operated at 37 ± 1 cycles per minute.

7.2 Brush—Replace the brush when the bristles have become worn to a point that the bristles extend less than 15 mm (3/4 in.) from the block. Mark the ends of the brush to ensure it is oriented in the same direction for each use.

7.2.1 Brushes (that are in frequent use)—Brushes that are in frequent use shall be stored in water. Each time before starting the first test of the day, remove the brush and rinse in water, then precondition the brush, by running it for 400 cycles on a scrub panel, after which it is ready for test work.

7.2.2 Brushes (that are not in regular use)—Brushes that will not be used on a regular basis shall be washed out thoroughly in water after their last use and stored with the bristling side up under ambient conditions. Before being used again, the brush should be soaked in water for at least 24 h. Precondition the brush as directed in 7.2.1 before starting the test work.

⁷ The sole source of supply of the Triton X-100 detergent known to the committee at this time is Union Carbide, 10235 W. Little York Road, Suite 300, Houston, TX 77040.

⁸ The sole source of supply of the Tamul 45, known to the committee at this time is Unimin Specialty Minerals Inc., 358 Elm St., New Canaan, CT 06840.

⁹ The sole source of supply of the 1,3,5-triethyl hexahydro-sym-triazine (Vandice TH), known to the committee at this time is R. T. Vanderbilt Co., 30 Winfield St., Norwalk, CT 06855.

Exhibit A (P.3 of 4)

7.3 Brush Holder—For washability testers that include a separate brush holder, insert a 3.2-mm (1/8-in.) thick rubber mat in the holder above the brush block. When in operation, this mat allows the brush to ride evenly on the paint surface without tilting. The brush must fit loosely in the holder. Mount the brush in the holder being sure that the mat is in place above the brush block and that the brush and holder are always in the same position.

TEST METHOD A

8. Procedure

8.1 Stir the test paint thoroughly and strain to remove all skins and particles. Make three drawdowns of each paint. Draw down the paint on the black plastic panel using the same operator and same 0.18-mm (7.0-mil) clearance film applicator. The time for application should be fairly slow—3 to 4 s from end to end to prevent formation of pinholes or holidays in the film. Air dry in a horizontal position for 7 days in an conditioning chamber at $23 \pm 2^\circ\text{C}$ ($73.5 \pm 3.5^\circ\text{F}$) and $50 \pm 5\%$ relative humidity in accordance with Specification D 3924.

8.2 Soak the brush in water overnight. Clean the plate and set it in the pan of the washability tester. Ensure that the shim is smooth and free of burrs and placed perpendicular to the path of the brush. Wipe the test panel carefully and place it on top of the shimmed plate with the painted side up. Be sure that there are no defects in the film above the shim and that the test area is level. Place the frame over the drawdown being sure that the entire gasket is on the painted surface. Clamp the gasket in place. The clamps should be tight enough to ensure close contact, but not tight enough to cause warping of the panel.

8.3 Before beginning the test, it should be noted that the brush has been preconditioned for 400 cycles as outlined in 7.2.1. Remove the brush and shake vigorously to remove any excess water. Stir the abrasive scrub medium and spread 10 g uniformly over the brush bristles. Place the brush at one end of the path. Wet the panel with 5 mL of water in the path of the brush.

8.4 Start the test. After each 400 cycles before failure, remove the brush (do not rinse), add 10 g of stirred abrasive scrub medium and place 5 mL of water on the path of the brush before continuing.

8.5 Record the number of cycles to remove one continuous thin line of paint film across the 12.7-mm (1/2-in.) width of the shim. Stop the machine and wipe off the shim area to determine, if necessary, if the end point is achieved.

8.6 Test two of the drawdowns. If the two results differ by more than 30 % of the average, test the third drawdown. If one of the three results is obviously discrepant, discard it, then average the results from the remaining drawdowns.

TEST METHOD B

9. Procedure

9.1 Stir the test paint and reference paint thoroughly and strain to remove all skins and particles. Draw down the test and reference paints side by side perpendicular to the length of the

panel following procedures outlined in 8.1. Prepare three drawdowns for each test/reference paint. The paints should be drawn down simultaneously and the painted portion should be in the middle of the chart. Air dry in a horizontal position for 7 days at standard conditions.

9.2 Soak the brush in water overnight. Clean the plate and set it in the pan of the washability machine. Centrally place two shims, one each under the test paint and one under the reference paint drawdown areas on the chart. Wipe the test panel carefully and place it on top of the shimmed plate with the painted side up. Be sure that there are no defects in the film above the shims and that the test areas are level. Place the gasket over the painted surface and clamp in place.

9.3 Remove the brush and shake it vigorously to remove any excess water. Before testing, the brush shall be conditioned for 400 cycles as outlined in 7.2.1. Follow procedures outlined in 8.3 and 8.4. It is recommended that the first two panels to be tested are prepared by altering the position of the reference paint, that is, one panel has the reference paint on the right, and the second panel has the reference paint on the left.

9.4 Record respectively the number of cycles to remove one continuous thin line of paint film from both the test and reference paints across the 12.7-mm (1/2-in.) width of each of the shims. Stop the machine and wipe off the shim areas to determine, if necessary, if each end point is achieved.

9.5 Test two of the drawdowns. If the two results differ by more than 30 %, test the third drawdown. If one of the three results is obviously discrepant, discard it, then average the results from the remaining drawdowns.

10. Report

10.1 Report the following information:

10.1.1 When using Test Method A, report the mean number of cycles to failure.

10.1.2 When using Test Method B, report a percentage as follows:

$$\frac{\text{Cycles for test paint}}{\text{Cycles for reference paint}} \times 100 \quad (1)$$

if:

Result is $> 100\%$, test paint has better scrub resistance than reference paint.

if:

Result is $< 100\%$, test paint has poorer scrub resistance than reference paint.

10.1.3 Method used (Test Method A or Test Method B).

10.1.4 Referenced paint used, if using Test Method B.

10.1.5 Outline any deviations from standard procedures.

11. Precision and Bias

11.1 Precision—In an interlaboratory study of these test methods, scrub resistance was recorded in five laboratories using three coatings. The following criteria should be used for judging the acceptability of results of scrub resistance tests at a 95 % confidence level.

Test Method A

11.1.1 Repeatability—Duplicate results by a single operator should be considered suspect if they differ by more than 30 % of their mean value.

~~Exhibit A (Page 4 of 4)~~

11.1.2 Reproducibility—Two results (each the mean of duplicate measurements) obtained by operators in different laboratories should be considered suspect if they differ by more than 58 % of their mean.

11.2 Bias—Bias is not applicable to these test methods.

12. Keywords

12.1 scrub resistance; wet abrasion resistance

Test Method B

11.1.3 Repeatability and reproducibility are being determined by ASTM D01.42.25.

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APPENDIX D

United State Patent Application Publication

Publication No.: US 2004/0102568 A1

Publication Date: May 27, 2004



US 20040102568A1

(19) **United States**(12) **Patent Application Publication** (10) Pub. No.: US 2004/0102568 A1
Bridgewater et al. (43) Pub. Date: May 27, 2004(54) **AQUEOUS COATING COMPOSITION****Publication Classification**(76) Inventors: **Brian Michael Bridgewater**,
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Norristown, PA (US)(51) Int. Cl.⁷ **C08K 3/00**
(52) U.S. Cl. **524/556**(57) **ABSTRACT**Correspondence Address:
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100 INDEPENDENCE MALL WEST
PHILADELPHIA, PA 19106-2399 (US)(21) Appl. No.: 10/700,076
(22) Filed: Nov. 3, 2003**Related U.S. Application Data**(60) Provisional application No. 60/428,420, filed on Nov.
22, 2002.

An aqueous coating composition including a pigment and an aqueous acrylic emulsion polymer including, as copolymerized units, from 50% to 99.75% by weight, based on dry polymer weight, monoethylenically unsaturated nonionic (meth)acrylic monomer and from 0.25% to 10% by weight, based on dry polymer weight, monoethylenically unsaturated acid monomer, the polymer having a Tg of -10° C. to 35° C. wherein the emulsion polymer is formed by a certain emulsion polymerization process at a temperature of from 70° C. to 99° C. in the presence of a thermal initiator is provided. Further provided is a method for forming a dry coating therefrom.

AQUEOUS COATING COMPOSITION

[0001] This invention relates to an aqueous coating composition including a pigment and an aqueous acrylic emulsion polymer. More particularly, this invention relates to an aqueous coating composition including a pigment and an aqueous acrylic emulsion polymer including, as copolymerized units, from 50% to 99.75% by weight, based on dry polymer weight, monoethylenically unsaturated nonionic (meth)acrylic monomer and from 0.25% to 10% by weight, based on dry polymer weight, monoethylenically unsaturated acid monomer, the polymer having a Tg of -10°C . to 35°C ., wherein the emulsion polymer is formed by emulsion polymerization at a temperature of from 70°C . to 99°C . in the presence of a thermal initiator, wherein the initiator is used in the amount of 0.3% to 0.4%, by weight, based on dry polymer weight, and wherein less than 0.15% by weight, based on dry polymer weight, of the initiator is present during the first 10%, by weight, based on dry polymer weight, of the conversion of monomers to the emulsion polymer; 0.001 to 0.05 moles of chain transfer agent/kg monomer; and a neutralizer, wherein the neutralizer is used in the amount of from 5% to 75%, on an equivalents basis, based on the monoethylenically unsaturated acid monomer, and wherein less than half of the neutralizer is present during the first 25%, by weight, based on dry polymer weight, of the conversion of monomers to the emulsion polymer. In an alternative aspect the invention relates to an aqueous coating composition in which the emulsion polymer is formed by emulsion polymerization at a temperature of from 70°C . to 99°C . in the presence of a thermal initiator, wherein the initiator is used in the amount of 0.05% to 0.3%, by weight, based on dry polymer weight, and wherein less than half of the initiator is present during the first 10%, by weight, based on dry polymer weight, of the conversion of monomers to the emulsion polymer, and a neutralizer, wherein the neutralizer is used in the amount of from 5% to 75%, on an equivalents basis, based on the monoethylenically unsaturated acid monomer, and wherein less than half of the neutralizer is present during the first 25%, by weight, based on dry polymer weight, of the conversion of monomers to the emulsion polymer. The invention also relates to a method for providing a dry coating composition of the previous description and a substrate bearing the coating.

[0002] The present invention serves to provide a dry coating including a predominantly acrylic emulsion polymer binder of a certain composition prepared by a particular free-radical thermal initiation process which coating exhibits at least one of improved scrub resistance and improved dirt pick-up resistance by which is meant herein improved relative to that of dry coatings which incorporate acrylic emulsion polymers of the same composition but are not so prepared.

[0003] PCT Patent Application WO 01/14426 discloses a process for preparing an aqueous polymer dispersion for use as a pressure-sensitive adhesive by free-radical emulsion polymerization in the presence of at least one initiator whereby at least 80% of the monomers and at least 75% of the initiator of the polymerization reaction are continuously added during the polymerization process.

[0004] Scrub resistance and dirt pick-up resistance are generally recognized desirable characteristics of a coating. The problem faced by the inventors is the provision of a

suitable aqueous coating composition, and a method for providing a dry coating therefrom so that a useful level of one or both of these properties can be effected. Alternative effective polymerization processes to achieve this end are desired. We have now found that certain aqueous acrylic emulsion polymer compositions prepared by a particular thermally-initiated process provide useful properties.

[0005] In a first aspect of the present invention there is provided an aqueous coating composition comprising a pigment and an aqueous acrylic emulsion polymer comprising, as copolymerized units, from 50% to 99.75% by weight, based on dry polymer weight, monoethylenically unsaturated nonionic (meth)acrylic monomer and from 0.25% to 10% by weight, based on dry polymer weight, monoethylenically unsaturated acid monomer, said polymer having a Tg of -10°C . to 35°C . wherein said emulsion polymer is formed by emulsion polymerization at a temperature of from 70°C . to 99°C . in the presence of a thermal initiator, wherein said initiator is used in the amount of 0.3% to 0.4%, by weight, based on dry polymer weight, and wherein less than 0.15% by weight, based on dry polymer weight, of said initiator is present during the first 10%, by weight, based on dry polymer weight, of the conversion of monomers to said emulsion polymer; 0.001 to 0.05 moles of chain transfer agent/kg monomer; and a neutralizer, wherein said neutralizer is used in the amount of from 5% to 75%, on an equivalents basis, based on said monoethylenically unsaturated acid monomer, and wherein less than half of said neutralizer is present during the first 25%, by weight, based on dry polymer weight, of the conversion of monomers to said emulsion polymer.

[0006] In a second aspect of the present invention there is provided an aqueous coating composition comprising a pigment and an aqueous acrylic emulsion polymer comprising, as copolymerized units, from 50% to 99.75% by weight, based on dry polymer weight, monoethylenically unsaturated nonionic (meth)acrylic monomer and from 0.25% to 10% by weight, based on dry polymer weight, monoethylenically unsaturated acid monomer, said polymer having a Tg of -10°C . to 35°C . wherein said emulsion polymer is formed by emulsion polymerization at a temperature of from 70°C . to 99°C . in the presence of a thermal initiator, wherein said initiator is used in the amount of 0.05% to 0.3%, by weight, based on dry polymer weight, and wherein less than half of said initiator is present during the first 10%, by weight, based on dry polymer weight, of the conversion of monomers to said emulsion polymer, and a neutralizer, wherein said neutralizer is used in the amount of from 5% to 75%, on an equivalents basis, based on said monoethylenically unsaturated acid monomer, and wherein less than half of said neutralizer is present during the first 25%, by weight, based on dry polymer weight, of the conversion of monomers to said emulsion polymer.

[0007] In a third aspect of the present invention there is provided a method for forming a dry coating incorporating the aqueous coating composition of the first and second aspect of the present invention.

[0008] In a fourth aspect of the present invention there is provided a substrate bearing the dry coating.

[0009] The aqueous coating composition of this invention includes at least one pigment. By "pigment" herein is meant a solid particulate material. The particulate material can be

inorganic or organic, or both, in nature. Included are materials known in the art as pigments, opacifying pigments, extenders, and the like. Suitable inorganic pigments include, for example, titanium dioxide, zinc oxide, iron oxide, clay, talc, calcium carbonate, magnesium silicate, and mica. Suitable organic pigments include, for example, polystyrene beads, polyethylene particles, and polymeric particles including a void such as Ropaque™ opaque polymers (Rohm and Haas Company, Philadelphia, Pa.). The amount of pigment in the aqueous coating composition can vary from a pigment volume concentration (PVC) of 1 to 85 and thereby encompass coatings otherwise described in the art, for example, as flat coatings, satin coatings, semi-gloss coatings, high gloss coatings, primers, textured coatings, and the like. The pigment volume concentration is calculated by the following formula:

$$PVC (\%) = \frac{\text{volume of pigment(s)} + \text{volume extender(s)}}{\text{total dry volume of paint}} \times 100.$$

[0010] The typical PVC of different optional sheen levels are set out below.

Sheen of Dry Coating	PVC (%)
gloss	15-30
semi-gloss	23-30
eggshell, satin, or low lustre	30-38
flat	38-85

[0011] The aqueous coating composition of this invention includes at least one aqueous acrylic emulsion polymer. The aqueous acrylic emulsion polymer contains, as copolymerized units, from 50% to 99.75% by weight, based on dry polymer weight, monoethylenically-unsaturated nonionic (meth)acrylic monomer including esters, amides, and nitriles of (meth)acrylic acid, such as, for example, (meth)acrylic ester monomer including methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, decyl acrylate, lauryl acrylate, stearyl acrylate, methyl methacrylate, butyl methacrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate, uriedo(meth)acrylate; (meth)acrylonitrile and (meth)acrylamide. The use of the term "(meth)" followed by another term such as acrylate, acrylonitrile, or acrylamide, as used throughout the disclosure, refers to both acrylate, acrylonitrile, or acrylamide and methacrylate, methacrylonitrile, and methacrylamide, respectively. By "nonionic monomer" herein is meant that the copolymerized monomer residue does not bear an ionic charge between pH=1-14.

[0012] The aqueous emulsion polymer contains, as copolymerized units, from 0.25% to 10% by weight, based on dry polymer weight, monoethylenically-unsaturated acid monomer such as, for example, acrylic acid, methacrylic acid, crotonic acid, itaconic acid, sulfoethyl methacrylate, phosphoethyl methacrylate, fumaric acid, maleic acid, monomethyl itaconate, monomethyl fumarate, monobutyl fumarate, and maleic anhydride. Preferably, the emulsion polymer contains, as copolymerized units, from 0.3% to 2.5% by weight, based on dry polymer weight, (meth)acrylic acid.

[0013] The aqueous emulsion polymer further contains, as copolymerized units, from 0 to 49.75% by weight, based on dry polymer weight, of optional monomers which are neither nonionic monoethylenically-unsaturated nonionic (meth)acrylic monomers nor monoethylenically-unsaturated acid monomers. Optional monomers include, for example, styrene or alkyl-substituted styrenes; butadiene; aminoalkyl(meth)acrylate, N-alkyl aminoalkyl(meth)acrylate, N,N-di-alkyl aminoalkyl(meth)acrylate; vinyl acetate, vinyl propionate, or other vinyl esters; vinyl monomers such as vinyl chloride, vinylidene chloride, and N-vinyl pyrrolidone; allyl methacrylate, vinyl toluene, vinyl benzophenone, diallyl phthalate, 1,3-butylene glycol dimethacrylate, 1,6-hexandioldiacrylate, and divinyl benzene.

[0014] The emulsion polymer used in this invention is substantially uncrosslinked, when it is applied to a substrate in the method of this invention, although low levels of deliberate or adventitious crosslinking can be present. When low levels of precrosslinking or gel content are desired low levels of optional nonionic multi-ethylenically unsaturated monomers such as, for example, 0.1%-5%, by weight based on the dry polymer weight, can be used. It is important, however, that the quality of the film formation is not materially impaired.

[0015] The polymerization techniques used to prepare the acrylic emulsion polymer of this invention are well known in the art. Conventional emulsion polymerization surfactants can be used such as, for example, anionic and/or nonionic emulsifiers such as, for example, alkali metal or ammonium salts of alkyl, aryl, or alkylaryl sulfates, sulfonates or phosphates; alkyl sulfonic acids; sulfosuccinate salts; fatty acids; ethylenically unsaturated surfactant monomers; and choxylated alcohols or phenols. Polymerizable surfactants can also be used. Preferred polymerizable surfactant monomers are nonylphenoxy propenyl polyethoxylated sulphate (for example as Hitenol from Dai-ichi Corp); sodium alkyl allyl sulphosuccinate (for example as Trem LF-40 from Henkel Corp); ammonium di-(tricyclo(5.2.1.0 2,6)dec-3-en-(8 or 9)oxyethyl)sulfosuccinate; and ammonium di-(tricyclo(5.2.1.0 2,6)dec-3-en-(8 or 9)sulfosuccinate. Additionally, the ammonium and metal salts of unsaturated C₆ to C₃₀ organic acids can be used, alone or in combination with the above surfactants. Examples of these acids are: alpha methyl cinnamic acid, alpha phenyl cinnamic acid, oleic acid, linoleic acid (as described in U.S. Pat. No. 5,362,832), ricinoleic acid, the unsaturated fraction of Tall oil rosin and fatty acids, disproportionated rosin acid, soybean oil fatty acids, olive oil fatty acids, sunflower oil fatty acids, linseed oil fatty acids, safflower oil fatty acids, sorbitol mono-oleate, abietic acid, poly(oxyethylene) sorbitol sesquiolate, and Empol 1010 Dimer Acid. Suitable polymerizable surfactant monomers also include, for example, maleate derivatives (as described in U.S. Pat. No. 4,246,387), and allyl derivatives of alkyl phenol ethoxylates (as described in JP-62227435). The amount of surfactant used is typically from 0.1% to 6% by weight, based on the total weight of monomer.

[0016] In the preparation of the aqueous acrylic emulsion polymer a thermal initiation process is used. The thermal initiator provides free radicals at a useful rate at the reaction temperature. The reaction temperature is maintained at a temperature from 70° C. to 99° C. throughout the course of the reaction. Preferred is a reaction temperature between 75°

C. and 95° C., more preferably between 80° C. and 90° C. The reaction temperature can be held at a constant temperature or varied throughout part or all of the reaction as desired. The reaction is typically carried out a pH of from 4 to 8. The monomer mixture can be added neat or as an emulsion in water. The monomer mixture can be added in one or more additions or continuously, linearly or not, over the reaction period, or combinations thereof. The thermal initiator provides free radicals at a useful rate at the reaction temperature. Useful initiators include, for example, sodium persulfate, potassium persulfate, ammonium persulfate, sodium perborate, and ammonium or alkali metal peroxydisulfate salts. Preferred are persulfate salts. The thermal initiation can be augmented by a minor amount of a redox initiated reaction which is effected when the thermal initiator, also known in the art as an oxidant, is contacted with a reductant. Suitable reductants include, for example, sodium sulfoxylate formaldehyde, alkali metal and ammonium salts of sulfur-containing acids, such as sodium sulfite, bisulfite, thiosulfate, hydrosulfite, sulfide, hydrosulfide or dithionite, formadinesulfonic acid, hydroxymethanesulfonic acid, acetone bisulfite, amines such as ethanolamine, glycolic acid, glyoxylic acid hydrate, ascorbic acid, isoascorbic acid, lactic acid, glyceric acid, malic acid, 2-hydroxy-2-sulfinoacetic acid, tartaric acid and salts of the preceding acids. Redox reaction catalyzing metal salts of iron, copper, manganese, silver, platinum, vanadium, nickel, chromium, palladium, or cobalt can optionally be used. In any event the reaction includes less than 0.5 moles, preferably less than 0.2 moles, more preferably less than 0.1 mole, and most preferably no moles of reductant per mole of thermal initiator. In the first aspect of this invention the thermal initiator is used in the amount of from 0.3% to 0.4%, by weight, based on dry polymer weight, and less than 0.15% by weight, based on dry polymer weight, of the initiator is present during the first 10%, by weight, based on dry polymer weight, of the conversion of monomers to emulsion polymer. In the second aspect of this invention the thermal initiator is used in the amount of from 0.05% to 0.3%, by weight, based on dry polymer weight, and less than half of the initiator is present during the first 10%, by weight, based on dry polymer weight, of the conversion of monomers to the emulsion polymer. In the preparation of the aqueous acrylic emulsion polymer a neutralizer is included. By "neutralizer" herein is meant is a basic material which is capable of entering into an acid-base reaction with the acid monomer. Suitable neutralizers include, for example, sodium hydroxide, potassium carbonate, and sodium bicarbonate. The neutralizer is used in the amount of from 5% to 75%, preferably from 5% to 50%, on an equivalents basis, based on the equivalents of monoethylenically unsaturated acid monomer, and less than half of the neutralizer is present during the first 25%, by weight, based on dry polymer weight, of the conversion of monomers to the emulsion polymer.

[0017] A chain transfer agent such as, for example, isopropanol, halogenated compounds, n-butyl mercaptan, n-amyl mercaptan, n-dodecyl mercaptan, t-dodecyl mercaptan, alkyl thioglycolate, mercaptopropionic acid, and alkyl mercaptoalkanoate in an amount of from 0.001 to 0.05, preferably from 0.0025 to 0.05 moles per kg dry polymer weight, is used in the first aspect of this invention. In the second aspect of this invention chain transfer agent is not required but in some embodiments it is used in an amount of

from 0.001 to 0.05, preferably from 0.0025 to 0.05, moles per kg dry polymer weight. Linear or branched C₄-C₂₂ alkyl mercaptans such as n-dodecyl mercaptan and t-dodecyl mercaptan are preferred. Chain transfer agent(s) can be added in one or more additions or continuously, linearly or not, over most or all of the entire reaction period or during limited portion(s) of the reaction period such as, for example, in the kettle charge and in the reduction of residual monomer stage.

[0018] The aqueous acrylic emulsion polymer has an average particle diameter of from 20 to 1000 nanometers, preferably from 70 to 300 nanometers. Particle sizes herein are those determined using a Brookhaven Model BI-90 particle sizer manufactured by Brookhaven Instruments Corporation, Holtsville N.Y., reported as "effective diameter". Also contemplated are multimodal particle size emulsion polymers wherein two or more distinct particle sizes or very broad distributions are provided as is taught in U.S. Pat. Nos. 5,340,858; 5,350,787; 5,352,720; 4,539,361; and 4,456,726.

[0019] The glass transition temperature ("Tg") of the aqueous acrylic emulsion polymer is typically from -10° C. to 35° C., preferably from 0° C. to 30° C., the monomers and amounts of the monomers selected to achieve the desired polymer Tg range are well known in the art. Tgs used herein are those calculated by using the Fox equation (T. G. Fox, Bull. Am. Physics Soc., Volume 1, Issue No. 3, page 123(1956)), that is, for calculating the Tg of a copolymer of monomers M1 and M2,

$$1/Tg(calc.) = w(M1)/Tg(M1) + w(M2)/Tg(M2)$$

[0020] , wherein

[0021] Tg(calc.) is the glass transition temperature calculated for the copolymer

[0022] w(M1) is the weight fraction of monomer M1 in the copolymer

[0023] w(M2) is the weight fraction of monomer M2 in the copolymer

[0024] Tg(M1) is the glass transition temperature of the homopolymer of M1

[0025] Tg(M2) is the glass transition temperature of the homopolymer of M2,

[0026] all temperatures being in ° K.

[0027] The glass transition temperatures of homopolymers are found, for example, in "Polymer Handbook", edited by J. Brandrup and E. H. Immergut, Interscience Publishers.

[0028] In one embodiment of the present invention the aqueous acrylic emulsion polymer is prepared by a multi-stage emulsion polymerization process, in which at least two stages differing in composition are polymerized in sequential fashion. Such a process usually results in the formation of at least two mutually incompatible polymer compositions, thereby resulting in the formation of at least two phases within the polymer particles. Such particles are composed of two or more phases of various geometries such as, for example, core/shell or core/sheath particles, core/shell particles with shell phases incompletely encapsulating the core, core/shell particles with a multiplicity of cores, and interpenetrating network particles. In all of these cases the majority of the surface area of the particle will be occupied

by at least one outer phase and the interior of the particle will be occupied by at least one inner phase. Each of the stages of the multi-staged emulsion polymer can contain the same monomers, surfactants, redox initiation system, chain transfer agents, etc. as disclosed hereinabove for the emulsion polymer. In the case of a multi-staged polymer particle at least one of the stages shall meet the description of the aqueous emulsion polymer of the first or second aspect of this invention. The polymerization techniques used to prepare such multistage emulsion polymers are well known in the art such as, for example, U.S. Pat. Nos. 4,325,856; 4,654,397; and 4,814,373.

[0029] In one embodiment of the present invention the aqueous acrylic emulsion polymer includes, as copolymerized units, from 50% to 99.65% by weight, based on dry polymer weight, monoethylenically unsaturated nonionic (meth)acrylic monomer, from 0.1% to 12.5% by weight, based on dry polymer weight, aldehyde reactive group-containing monomer, and from 0.25% to 10% by weight, based on dry polymer weight, monoethylenically unsaturated acid monomer, the polymer having a Tg of -10° C. to 35° C., and is formed according to either the first or second aspects of this invention. By "aldehyde reactive group-containing monomer" is meant herein a monomer which, in a homogeneous solution containing 20% by weight of the monomer and an equimolar amount of formaldehyde at any pH from 1 to 14, will exhibit greater than 10% extent of reaction between the monomer and formaldehyde on a molar basis in one day at 25° C. Included as ethylenically-unsaturated aldehyde reactive group-containing monomers are, for example, vinyl acetoacetate, acetoacetoxyethyl (meth)acrylate, acetoacetoxypropyl(meth)acrylate, allyl acetoacetate, acetoacetoxybutyl(meth)acrylate, 2,3-di(acetoacetoxy)propyl(meth)acrylate, vinyl acetoacetamide, acetoacetoxyethyl(meth)acrylamide, 3-(2-vinyl-oxyethylamino)-propionamide, N-(2-(meth)acryloxyethyl)-morpholinone-2, 2-methyl-1-vinyl-2-imidazoline, 2-phenyl-1-vinyl-2-imidazoline, 2-(3-Oxazolidinyl)ethyl(meth)acrylate, N-(2-vinyl-oxyethyl)-2-methyloxazolidine, 4,4-dimethyl-2-isopropenyloxazoline, 3-(4-pyridyl)propyl(meth)acrylate, 2-methyl-5-vinyl-pyridine, 2-vinyl-oxyethylamine, 2-vinyl-oxyethyl-ethylene-diamine, 3-aminopropyl vinyl ether, 2-amino-2-methylpropyl vinyl ether, 2-aminobutyl vinyl ether, tert-butylaminoethyl(meth)acrylate, 2-(meth)acryloxyethyl-dimethyl- β -propiocarbonate, diethanolamine monovinyl ether, o-aniline vinyl thioether, (meth)acryloxyacetamido-ethyl-ethyleneurea, ethyleneureidoethyl(meth)acrylate, (meth)acrylamidoethyl-ethyleneurea, (meth)acrylamidoethyl-ethylenethiourea, N-((meth)acrylamidoethyl)-N¹-hydroxymethyl-ethyleneurea, N-((meth)acrylamidoethyl)-N¹-methoxymethyl-ethyleneurea, N-formamidoethyl-N¹-vinylethyleneurea, N-vinyl-N¹-aminooethyl-ethyleneurea, N-(ethyleneureidoethyl)-4-pentenamide, N-(ethyleneureidoethyl)-10-undecenamide, butyl ethyleneureido-ethyl fumarate, methyl ethyleneureido-ethyl fumarate, benzyl N-(ethyleneureidoethyl)fumarate, benzyl N-(ethyleneureidoethyl)maleamate, N-vinyl-oxyethyl-ethyleneurea, N-(ethyleneureidoethyl)-crotonamide, ureidopenyl vinyl ether, 2-ureidoethyl (meth)acrylate, N-2-(allylcarbamato)aminoethyl imidazolidinone, 1-(2-(20-hydroxy-3-(2-propenyloxy)propyl)amino)ethyl-2-imidazolidinone, hydrogen ethyleneureidoethyl itaconamide, ethyleneureidoethyl hydrogen itaconate, bis-ethyleneureidoethyl itaconate, ethyleneureidoethyl undecylenate,

ethyleneureidoethyl undecylenamide, 2-(3-methylolimidazolidone-2-yl-1)ethyl acrylate, N-acryloxyalkyl oxazolidines, acylamidoalkyl vinyl alkyleneureas, aldehyde-reactive amino group-containing monomers as dimethylaminoethyl methacrylate, and ethylenically unsaturated monomers containing aziridine functionality. Preferred is from 0.25% to 5%, by weight based on total monomer weight, of a copolymerized ethylenically-unsaturated aldehyde reactive group-containing monomer, based on the weight of the polymer.

[0030] In an alternative embodiment aqueous acrylic emulsion polymers containing a sufficient amount of copolymerized monomer(s) having reactive functionality, which is not reactive with aldehydes, to provide, after reaction during or after the emulsion polymerization, from 0.1% to 12.5%, by weight based on the total weight of the emulsion polymer, copolymerized aldehyde-reactive monomer equivalent are also contemplated. By "copolymerized monomer equivalent" is meant herein the copolymerized monomer which would have led to the copolymer even though the polymer was formed by a post-polymerization reaction rather than directly formed by the copolymerization of that monomer. In this embodiment, for example, the reaction product of polymers containing carboxylic acid functionality with compounds consisting of or containing an aziridine (ethyleneimine) ring or rings can be formed. Substitution on the ring can be on the nitrogen and/or either or both carbons such as, for example, ethyleneimine, propyleneimine, N-(2-hydroxyethyl) ethyleneimine, trimethylolpropane-tris-(β -(N-aziridinyl)propionate), and pentaerythritol trimethylolpropane-tris-(β -(N-aziridinyl)propionate). Also, polymers containing β -aminoester and/or β -hydroxyamide functionality can be formed by post-polymerization processes.

[0031] In another embodiment of this invention improved adhesion of a dry coating to an alkyd substrate, particularly to an aged or weathered alkyd-coated substrate, when the aqueous coating composition includes a second emulsion polymer which provides a coating with inferior adhesion such as, for example, a colloidal-stabilized emulsion polymer, is provided. By "colloidally-stabilized" emulsion polymer herein is meant an emulsion polymer prepared, at least in part, in the presence of a nonionic colloidal stabilizer. Without being bound by a particular theory, it is believed that such a process results in the grafting of at least part of the colloidal stabilizer on the emulsion polymer with beneficial effect on the rheology of coatings prepared therefrom but provides inferior adhesion. The aqueous coating composition including (1) a first aqueous emulsion polymer including from 0 to 2%, by weight based on the total weight of the first polymer, ethylenically unsaturated aldehyde reactive group-containing monomer, the first polymer having a Tg of from -60° C. to 80° C. and a particle diameter of from 200 to 1000 nanometers, prepared, at least in part, in the presence of from 0.001% to 6%, by weight based on the dry weight of the first emulsion polymer, of a colloidal stabilizer selected from the group consisting of hydroxyethyl cellulose, N-vinyl pyrrolidone, polyvinyl alcohol, partially acetylated polyvinyl alcohol, carboxymethyl cellulose, gum arabic, and mixtures thereof, and (2) a second aqueous emulsion polymer that includes, as copolymerized units, from 50% to 99.65% by weight, based on dry polymer weight, monoethylenically unsaturated nonionic (meth)acrylic monomer, from 0.1% to 12.5% by weight, based on dry polymer weight, aldehyde reactive group-containing

monomer, and from 0.25% to 10% by weight, based on dry polymer weight, monoethylenically unsaturated acid monomer, the polymer having a T_g of from -10° C. to 35° C. and a particle diameter of from 30 nanometers to 200 nanometers, formed according to either the first or second aspects of this invention; wherein the dry weight ratio of the second polymer to that of the first polymer is from 1:99 to 1:1. This embodiment provides adhesion improved relative to that engendered when the colloidal-stabilized emulsion polymer is used without the second emulsion polymer (the aqueous emulsion polymer used in the coating composition of this invention) in a corresponding aqueous coating composition. Blending of the first emulsion polymer and the second emulsion polymer can be effected prior to or while formulating the binders in an aqueous coating composition.

[0032] In one embodiment the aqueous coating composition of this invention includes, in addition to a pigment and an aqueous acrylic emulsion polymer, as described hereinabove in the first and second aspects of this invention, from 2% to 40%, preferably from 3% to 25%, by weight, based on the total dry polymer weight, of a second emulsion polymer that has a T_g of from 25° C. to 150° C., wherein the T_g of the second polymer is at least 10° C., preferably at least 20° C., higher than the T_g of the aqueous acrylic emulsion polymer. In one version the second emulsion polymer has an average particle diameter that is larger, preferably from 2 to 5 times larger, than the average particle diameter of the aqueous acrylic emulsion polymer; coatings prepared from such a composition have enhanced scrub resistance. In another version the aqueous acrylic emulsion polymer has an average particle diameter that is larger, preferably from 2 to 5 times larger, than the average particle diameter of the second emulsion polymer; coatings prepared from such a composition have enhanced dirt pickup resistance. In a further version, the aqueous coating composition contains both a second emulsion polymer having an average particle diameter greater than that of the aqueous acrylic emulsion polymer and a second emulsion polymer having an average particle diameter smaller than that of the aqueous acrylic emulsion polymer; coatings formed from such a composition have a combination of improved dirt pickup resistance and improved scrub resistance compared to a coating containing either only one of the second emulsion polymers.

[0033] The aqueous coating composition of this invention is prepared by techniques which are well known in the coatings art. At least one pigment is well dispersed in an aqueous medium under high shear such as is afforded by a COWLES™ mixer or, in the alternative, at least one pre-dispersed pigment can be used. Then the acrylic emulsion polymer can be added under low shear stirring along with other coatings adjuvants as desired. Alternatively, the emulsion polymer can be present during the pigment dispersion step. The aqueous coating composition can contain conventional coatings adjuvants such as, for example, emulsifier, buffer or neutralizer in addition to the in-process neutralizer, coalescent, thickener or rheology modifier, freeze-thaw additive, wet-edge aid, humectant, wetting agent, biocide, antifoaming agent, UV absorber such as benzophenone, substituted benzophenones, and substituted acetophenones, colorant, wax, and anti-oxidant.

[0034] Preferably the aqueous coating composition contains less than 5% VOC by weight based on the total weight

of the coating composition; more preferably the aqueous coating composition contains less than 3% VOC by weight based on the total weight of the coating composition; even more preferably the aqueous coating composition contains less than 1.7% VOC by weight based on the total weight of the coating composition. A volatile organic compound ("VOC") is defined herein as a carbon-containing compound that has a boiling point below 280° C. at atmospheric pressure, compounds such as water and ammonia being excluded from VOCs.

[0035] A "low VOC" coating composition herein is a coating composition which contains less than 5% VOC by weight based on the total weight of the coating composition; preferably it contains from 0 to 1.7% by weight based on the total weight of the coating composition.

[0036] Frequently a VOC is deliberately added to a paint or coating to improve the film properties or to aid in coatings application properties. Examples are glycol ethers, organic esters, aromatic compounds, ethylene and propylene glycol, and aliphatic hydrocarbons. It is preferred that the coating composition contains less than 5% by weight based on the total weight of the coating composition of the added VOCs and more preferably less than 1.7% by weight based on the total weight of the coating composition of the added VOCs.

[0037] Additionally, the low VOC coating composition can contain coalescing agents which are not VOCs. A coalescing agent is a compound that is added to a water-borne emulsion polymer, paint or coating and which reduces the minimum film forming temperature (MFFT) of the emulsion polymer, paint or coating by at least 1° C. The MFFT is measured using ASTM test method D2354. Examples of a coalescing aid which is not a VOC include a plasticizer, low molecular weight polymer, and surfactants. That is, a non-VOC coalescing agent is a coalescing agent which has a boiling point above 280° C. at atmospheric pressure.

[0038] Typical methods of paint or coating preparation can introduce adventitious VOCs from the emulsion polymer, biocides, defoamers, soaps, dispersants, and thickeners. These typically account for 0.1% VOC by weight based on the total weight of the coating composition. Additional methods such as steam stripping and choice of low VOC containing additives like biocides, defoamers, soaps, dispersants, and thickeners, can be used to further reduce the paint or coating to less than 0.01% VOC by weight based on the total weight of the coating composition.

[0039] In a preferred embodiment the aqueous coating composition has a PVC of 15 to 38 and has less than 5% VOC by weight based on the total weight of the coating composition. In another preferred embodiment the aqueous coating composition has a PVC of greater than 38 and has less than 3% VOC by weight based on the total weight of the coating composition. In an additional embodiment the aqueous coating composition has a PVC of 15 to 85 and has less than 1.7% VOC by weight based on the total weight of the coating composition.

[0040] The solids content of the aqueous coating composition can be from 20% to 60% by volume. The viscosity of the aqueous coating composition can be from 50 KU (Krebs Units) to 120 KU as measured using a Brookfield Digital

viscometer KU-1; the viscosities appropriate for different application methods vary considerably.

[0041] Conventional coatings application methods such as, for example, brushing, rolling, and spraying methods such as, for example, air-atomized spray, air-assisted spray, airless spray, high volume low pressure spray, and air-assisted airless spray can be used in the method of this invention. The aqueous coating composition can be advantageously applied to substrates such as, for example, plastic, wood, metal, primed surfaces, previously painted surfaces, weathered painted surfaces and cementitious substrates. Drying is typically allowed to proceed under ambient conditions such as, for example, at 0° C. to 35° C., but drying at higher temperatures can also be effected.

[0042] The following examples are presented to illustrate the invention and the results obtained by the test procedures.

[0043] Test Procedures

[0044] Scrub Resistance: The Scrub Resistance was measured according to Test Method A of Standard Test Methods for Scrub Resistance of Wall Paints (ASTM Test Method D 2486-00).

[0045] Krebs Unit (KU) Viscosity Measurements: The KU viscosity was measured according to Method B of Standard Test Method for Consistency of Paints Measuring Krebs Unit (KU) Viscosity Using a Stormer-Type Viscometer (ASTM Test Method D 562-01).

[0046] High Shear (ICI) Viscosity Measurements: The ICI viscosity was measured according to Standard Test Method for High-Shear Viscosity Using and Cone/Plate Viscometer (ASTM Test Method D 4287-00).

[0047] Dirt Pickup Resistance: Aqueous coating compositions were drawn down on separate aluminum panels at a wet thickness of 0.0762 mm (3 mil) using a Bird film applicator 76.2 mm (3 inch) in width. The samples were allowed to dry at 21° C. (70° F.) and 50% relative humidity for 7 days. The samples were exposed in southern Florida at a commercial exposure station (Q-LAB Weathering Research Service, Homestead, Fla.). The exposure direction was south at a 45° angle. The colors of the dry coating samples were characterized by measuring initial values of L*, a*, and b* prior to exposure. After 90 days of exposure, the L*, a*, and b* values were remeasured to determine the changes in color of the dry coating samples. The changes in the values of L*, referred to as "ΔL*", are determined for the dry coating samples. A negative value for ΔL* indicated a darkening of the dry coating as a result of the pickup of dirt and other material on the dry coating surface.

[0048] The relative dirt pickup resistance was the ratio of the ΔL* value for the dry coating prepared from the comparative aqueous polymer composition divided by the ΔL* value for the dry coating prepared from the test composition. A relative dirt pickup resistance value, referred to as "RL", having a value of 1.1 or greater indicated improvement in the dirt pickup resistance.

[0049] The abbreviations listed below are used throughout the examples.

MAA =	Methacrylic Acid
BA =	Butyl Acrylate
MMA =	Methyl Methacrylate
VA =	Vinyl Acetate
n-DDM =	n-Dodecyl Mercaptan
SLS =	Sodium lauryl sulfate (28% active)
APS =	Ammonium persulfate
DI water =	Deionized water

EXAMPLE 1

Preparation of Aqueous Acrylic Emulsion Polymer

[0050] 20 g MAA, 480 g BA, 500 g MMA and 1.25 g n-DDM were combined with 455 g DI water and 30.5 g SLS (28%) and emulsified with stirring. 5.2 g SLS (28%) and 215 g DI water were charged to a 3 L multi-neck flask fitted with mechanical stirring. The flask contents were heated to 89° C. under nitrogen. To the stirred kettle contents were added 35 g monomer emulsion followed by 0.35 g sodium carbonate in 10 g DI water and 0.78 g APS in 10 g DI water. Gradual addition of the monomer emulsion was subsequently initiated. At the same time gradual addition of separate solutions of 2.72 g APS in 50 g DI water and 6.55 g sodium carbonate in 125 g DI water were started. Total addition time for all three feeds was 90-100 minutes. Reactor temperature was maintained at 85 to 88° C. throughout the polymerization. 20 g DI water was used to rinse the emulsion feed line to the reactor. After completion of the feeds the reactor was cooled to 60° C. 0.02 g ferrous sulfate heptahydrate and 0.02 g Tetrasodium salt of ethylenediamine-tetraacetic acid in 15.6 g DI water, 0.5 g t-butyl hydroperoxide and 0.25 g D-Isoascorbic acid in aqueous solutions were added. The polymer emulsion was neutralized to pH 9-10 with ammonium hydroxide.

COMPARATIVE EXAMPLE A

Preparation of Emulsion Polymer

[0051] 20 g MAA, 480 g BA, 500 g MMA and 1.25 g n-DDM were combined with 455 g DI water and 30.5 g SLS (28%) and emulsified with stirring. 5.2 g SLS (28%) and 310 g DI water were charged to a 3 L multi-neck flask fitted with mechanical stirring. The flask contents were heated to 89° C. under nitrogen. To the stirred kettle contents were added 35 g monomer emulsion followed by 6.9 g sodium carbonate in 40 g DI water and 0.78 g APS in 10 g DI water. Gradual addition of the monomer emulsion was subsequently initiated. At the same time gradual addition of 2.72 g APS in 50 g DI water was started. Total addition time for both feeds was 90-100 minutes. Reactor temperature was maintained at 85 to 88° C. throughout the polymerization. 20 g DI water was used to rinse the emulsion feed line to the reactor. After completion of the feeds the reactor was cooled to 60° C. 0.02 g ferrous sulfate heptahydrate and 0.02 g Tetrasodium salt of ethylenediamine-tetraacetic acid in 15.6 g DI water, 0.5 g t-butyl hydroperoxide and 0.25 g D-Isoascorbic acid in aqueous solutions were added. The polymer emulsion was neutralized to pH 9-10 with ammonium hydroxide.

COMPARATIVE EXAMPLE B

Preparation of Emulsion Polymer

[0052] This polymer was prepared according to Comparative Example A except that 2.72 g APS replaced 0.78 g APS

charged to reactor at beginning of polymerization and 0.78 g APS replaced 2.72 g APS in solution gradually fed to reactor.

EXAMPLE 2

Preparation of Aqueous Acrylic Emulsion Polymer

[0053] This polymer was prepared according to Example 1 except that 0.3 g APS replaced 0.78 g APS charged to reactor at beginning of polymerization and 1.05 g APS replaced 2.72 g APS in solution gradually fed to reactor.

COMPARATIVE EXAMPLE C

Preparation of Emulsion Polymer

[0054] This polymer was prepared according to Comparative Example A except that 0.3 g APS replaced 0.78 g APS charged to reactor at beginning of polymerization and 1.05 g APS replaced 2.72 g APS in solution gradually fed to reactor.

COMPARATIVE EXAMPLE D

Preparation of Emulsion Polymer

[0055] This polymer was prepared according to Comparative Example A except that 1.05 g APS replaced 0.78 g APS charged to reactor at beginning of polymerization and 0.3 g APS replaced 2.72 g APS in solution gradually fed to reactor.

EXAMPLE 3

Formation of Aqueous Coating Compositions

[0056] Aqueous coating compositions were made using the following formulation:

Material	Grams
Propylene Glycol	18.2
Pigment Dispersant (TAMOL™ 731)	6.45
Defoamer (FOAMASTER™ VL)	0.5
Titanium dioxide (TI-PURE™ R-900)	126.50
Water	31.0

[0057] The preceding ingredients were mixed in a high shear Cowles mixer and then the following ingredients were added with low shear mixing

Emulsion Polymer	232.29
Opaque Polymer (ROPAQUE™ ULTRA)	14.40
Coalescent (TEXANOL™)	4.83
Defoamer (FOAMASTER™ VL)	0.5
Rheology modifier (ACRYSOL™ RM-1020)	Table 4.1
Rheology modifier (ACRYSOL™ RM-825)	Table 4.1
Water	77.79

[0058] KU and ICI viscosity were adjusted to 90 to 95 and 1.4 to 2.1 respectively by the addition of the amounts of ACRYSOL™ RM-1020 and ACRYSOL™ RM-825 listed in the Table 4.1

TABLE 3.1

Rheology Modifier amounts		
Aqueous Coating Comp. Including Emulsion Pol.	ACRYSOL™ RM-1020	ACRYSOL™ RM-825
EXAMPLE 1	15.5 g	0.5 g
COMP. EX. A	17.8 g	4.7 g
COMP. EX. B	15.1 g	4.6 g
EXAMPLE 2	14.7 g	1.9 g
COMP. EX. C	16.0 g	5.8 g
COMP. EX. D	20.7 g	4.2 g

Note:

TAMOL, ROPAQUE and ACRYSOL are trademarks of Rohm and Haas Company, Philadelphia, PA.
FOAMASTER is a trademark of Henkel Corp., Gulph Mills, PA.
TI-PURE is a trademark of ICI DuPont de Nemours Co., Wilmington, DE.
TEXANOL is a trade mark of Eastman Chemical Co., Kingsport, TN.

EXAMPLE 4

Evaluation of Scrub Resistance

[0059] Dry coatings formed from aqueous coating compositions according to Example 3 including the aqueous emulsion polymers of Examples 1-2 and Comparative Examples A-D were evaluated for scrub resistance. Results are presented in Table 4.1.

TABLE 4.1

Scrub Resistance (Number of Scrubs)			
Criterion	First cut	Cut through	25% wear
EXAMPLE 1	829	920	1047
Comp. Ex. A	754	854	958
Comp. Ex. B	566	641	731
EXAMPLE 2	1065	1224	1437
Comp. Ex. C	730	836	900
Comp. Ex. D	697	742	831

[0060] Dry coating formed from the aqueous coating composition including the aqueous emulsion polymer of Example 1 exhibited scrub resistance superior to those including Comparative Examples A-B. Dry coating formed from the aqueous coating composition including the aqueous emulsion polymer of Example 2 exhibited scrub resistance superior to those including Comparative Examples C-D.

EXAMPLES 5-6 AND COMPARATIVE EXAMPLES E-II

Preparation of Aqueous Emulsion Polymers

[0061] Example 5 is made according to Example 2 with the exception that 10 g MMA is replaced with 10 g ureido methacrylate.

[0062] Comparative Example E is made according to Comparative Example C with the exception that 10 g MMA is replaced with 10 g ureido methacrylate.

[0063] Comparative Example F is made according to Comparative Example D with the exception that 10 g MMA is replaced with 10 g ureido methacrylate.

[0064] Example 6 is made according to Example 1 with the exception that 10 g MMA is replaced with 10 g ureido methacrylate.

[0065] Comparative Example G is made according to Comparative Example A with the exception that 10 g MMA is replaced with 10 g ureido methacrylate.

[0066] Comparative Example H is made according to Comparative Example B with the exception that 10 g MMA is replaced with 10 g ureido methacrylate.

EXAMPLE 7

Formation of Aqueous Coating Compositions

[0067] Aqueous coating compositions were made using the following formulation:

Material	Grams
Propylene Glycol	18.2
Pigment Dispersant (TAMOL™ 731)	6.45
Defoamer (FOAMASTER™ VI)	0.5
Titanium dioxide (TI-PURE™ R-900)	126.50
Water	31.0

[0068] The preceding ingredients were mixed in a high shear Cowles mixer and then the following ingredients were added with low shear mixing

Emulsion Polymer	232.29
Opaque Polymer (ROPAQUE™ ULTRA)	14.40
Coalescent (TEXANOL™)	4.83
Defoamer (FOAMASTER™ VI)	0.5
Rheology modifier (ACRYSOL™ RM-1020)	14.2
Rheology modifier (ACRYSOL™ RM-825)	0.25
Water	77.79

[0069] These aqueous coating compositions contain 4.4% VOC by weight based on the total weight of the coating composition.

EXAMPLE 8

Evaluation of Adhesion of Dry Coatings

[0070] Aqueous coating compositions are prepared according to Example 7 incorporating the aqueous emulsion polymers of Examples 5-6 and Comparative Examples E-H. The aqueous coating compositions are applied to a coating of Duron Superior House & Trim Exterior Alkyd House Paint—Forest Green Color (Manufactured by Duron, Inc., Beltsville, Md.) which has been painted onto a substrate and allowed to air dry and cure at room temperature for a period of 4 months. Adhesion to the alkyd substrate is measured by the method of ASTM 4541.

[0071] The adhesion of the dry aqueous coating composition containing the emulsion polymer of Example 5 is superior to that of Comparative Examples E-F. The adhesion of the dry aqueous coating composition containing the emulsion polymer of Example 6 is superior to that of Comparative Examples G-H.

EXAMPLE 9

Preparation and Evaluation of Dry Coatings Prepared from Aqueous Coating Composition Including a Pigment, an Aqueous Acrylic Emulsion Polymer, and a Second Emulsion Polymer

[0072] Preparation of second emulsion Polymer A monomer mixture was prepared by combining 413 g DI water, 16.4 g SLS, 495.6 g BA, 1285.0 g MMA, and 36.7 g MAA. Next, 1482 g DI water and 32.8 g SLS were added to a five liter flask equipped with mechanical stirring. The contents of the flask were heated to 85° C. A solution containing 5.7 g sodium carbonate dissolved in 56 g DI water was added to the flask, followed by 102 g of the monomer emulsion, followed by a solution containing 7.3 g ammonium persulfate dissolved in 51 g DI water. Next, 36.7 g of 50 weight % ureido methacrylate was added to the monomer emulsion. The remainder of monomer emulsion was added to the flask over a period of 90 minutes, while contents of the flask was maintained at a temperature in the range of 83-85° C. The flask contents were held at temperature for 10 minutes and then cooled to 65° C. Next 6.6 ppm ferrous sulfate, 1 g t-butyl hydroperoxide, and 0.5 g D-isoascorbic acid in aqueous solutions were added to the flask. After cooling to 45° C., the contents of the flask 16.0 g ammonium hydroxide (29% active) and DI water were added.

[0073] The second emulsion polymer contained 45.9 weight % solids with an average particle diameter of 102 nm and a Tg of 43° C.

[0074] Preparation of Aqueous Coating Compositions

[0075] Titanium dispersions are prepared by mixing the following ingredients in the order listed under high shear conditions.

Ingredient	Weight in grams
Tamol™ 731A dispersant (Rohm and Haas Co.)	13.99
Tego™ Foamex 810 defoamer (Th. Goldschmidt AG)	1.13
Surfynol™ CT-111 surfactant (Air Products)	2.25
Ti-Pure™ R-706 titanium dioxide (E. I. DuPont DeNemours Co.)	244.44
Water	62.26

[0076] The aqueous coating composition is prepared by adding the ingredients below in the order listed with low shear mixing.

Ingredient	Example 9	Comparative 1
titanium dioxide dispersion	344.07 g	344.07 g
Water	20.00 g	20.00 g
propylene glycol	16.50 g	16.50 g
Aqueous acrylic emulsion polymer of Example 2	430.1 g	537.65 g
Second emulsion polymer (as above)	115.26 g	—
Surfynol™ CT-111 surfactant	1.00 g	1.00 g
ammonia (28%)	0.70 g	0.70 g
Polyphase™ AIT-1 biocide (Froy Corporation)	8.00 g	8.00 g
Acrysol™ RM-2020 NPR rheology modifier (Rohm and Haas Co.)	29.00 g	29.00 g

-continued

Ingredient	Example 9	Comparative 1
Acrysol™ RM-8W rheology modifier (Rohm and Haas Co.)	5.60 g	5.60 g
water	104.2 g	113.62 g
VOC (weight %)	<2.25	<2.25

[0077] Evaluation of Dirt Pickup Resistance

[0078] Dry coatings are prepared from Example 9 and Comparative Example 1 and are evaluated according to the procedure for the dirt pickup resistance test. The dirt pickup resistance for the dry coating prepared from the aqueous coating composition of this invention is superior to that of the dry coating prepared from the Comparative Example.

What is claimed is:

1. An aqueous coating composition comprising a pigment and an aqueous acrylic emulsion polymer comprising, as copolymerized units, from 50 to 99.75% by weight, based on dry polymer weight, monoethylenically unsaturated non-ionic (meth)acrylic monomer and from 0.25 to 10% by weight, based on dry polymer weight, monoethylenically unsaturated acid monomer, said polymer having a glass transition temperature (T_g) of -10° C. to 35° C. wherein said emulsion polymer is formed by emulsion polymerization at a temperature of from 70° C. to 99° C. in the presence of a thermal initiator, wherein said initiator is used in the amount of 0.3% to 0.4%, by weight, based on dry polymer weight, and wherein less than 0.15% by weight, based on dry polymer weight, of said initiator is present during the first 10%, by weight, based on dry polymer weight, of the conversion of monomers to said emulsion polymer; 0.001 to 0.05 moles of chain transfer agent/kg monomer; and a neutralizer, wherein said neutralizer is used in the amount of from 5% to 75%, on an equivalents basis, based on said monoethylenically unsaturated acid monomer, and wherein less than half of said neutralizer is present during the first 25%, by weight, based on dry polymer weight, of the conversion of monomers to said emulsion polymer.

2. An aqueous coating composition comprising a pigment and an aqueous acrylic emulsion polymer comprising, as copolymerized units, from 50 to 99.75% by weight, based on dry polymer weight, monoethylenically unsaturated non-ionic (meth)acrylic monomer and from 0.25 to 10% by weight, based on dry polymer weight, monoethylenically unsaturated acid monomer, said polymer having a T_g of -10° C. to 35° C. wherein said emulsion polymer is formed

by emulsion polymerization at a temperature of from 70° C. to 99° C. in the presence of a thermal initiator, wherein said initiator is used in the amount of 0.05 to 0.3%, by weight, based on dry polymer weight, and wherein less than half of said initiator is present during the first 10%, by weight, based on dry polymer weight, of the conversion of monomers to said emulsion polymer, and a neutralizer, wherein said neutralizer is used in the amount of from 5% to 75%, on an equivalents basis, based on said monoethylenically unsaturated acid monomer, and wherein less than half of said neutralizer is present during the first 25%, by weight, based on dry polymer weight, of the conversion of monomers to said emulsion polymer.

3. The aqueous coating composition of claim 1 or claim 2 wherein said aqueous acrylic emulsion polymer comprises, as copolymerized units based on dry polymer weight, from 50% to 99.65% by weight monoethylenically unsaturated nonionic (meth)acrylic monomer, from 0.1% to 12.5% by weight aldehyde reactive group-containing monomer, and from 0.25% to 10% by weight monoethylenically unsaturated acid monomer.

4. The aqueous coating composition of claim 1 or claim 2 further comprising from 2% to 40% by weight, based on the total dry polymer weight, of a second emulsion polymer that has a T_g of from 25° C. to 150° C., wherein the T_g of said second polymer is at least 10° C. higher than the T_g of said aqueous acrylic emulsion polymer.

5. The aqueous coating composition of claim 1 or claim 2 having a PVC of 15 to 38 and having VOC less than 5% by weight based on the total weight of the coating composition.

6. The aqueous coating composition of claim 1 or claim 2 having a PVC greater than 38 and having VOC less than 3% by weight based on the total weight of the coating composition.

7. The aqueous coating composition of claim 1 or claim 2 having a PVC of 15 to 85 and having VOC less than 1.7% by weight based on the total weight of the coating composition.

8. A method for forming a dry coating comprising:

- forming the aqueous coating composition of claim 1 or claim 2;
- applying said coating composition to a substrate; and
- drying, or allowing to dry, said applied coating composition.

9. A substrate bearing the dry coating formed by the method of claim 8.

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